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Reactive Extrusion of Recycled Bottle Waste Material

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The objective of this study is to investigate the effect of reactive processing of commingled bottle waste polymer in an extruder. A variety of peroxides and monomers were tested to assess their influence on the final mechanical properties of the product. The reactive extruded polymer blends were prepared in two types of extruders: a co-rotating twin-screw extruder and a Buss co-Kneader single-screw extruder. Blends were analyzed for mechanical and thermal properties. The effectiveness of the different monomers and peroxides was evaluated in terms of improvement in impact properties. It has been found that the toughness of the polymer blend is improved by reactive processing. Depending on the amount and type of reactants, the impact strength can be improved by 220%, with a slight reduction in the modulus compared to an unmodified physical blend. The most suitable monomers were n-butylmethacrylate (BMA), t-butylamino ethylmethacrylate (TBAEMA) and a combination of styrene/maleic anhydride (ST/MAH). The peroxide should have a short half-lifetime compared to the average residence time in the extruder. The most effective monomers have a high initial reactivity and low rate of evaporation at the processing conditions used. Changes in processing conditions in the extruder influence the reaction conditions and therefore the final properties of the blend. Results were interpreted in terms of residence time, melting profile and peroxide concentration.

INTRODUCTION

A major part of polymer waste consists of polyolefins and especially high-density polyethylene (HDPE). HDPE is the primary material for blow molded bottles for milk, water, detergents or shampoo, which account for 40% of the total use of HDPE. Usually, HDPE waste streams are commingled with other polymers, for example polypropylene (PP) from spouts or closures. Because polyethylene and polypropylene are considered incompatible, the presence of PP will lead to poor mechanical properties that are below the weighted average of the pure components. Contamination of waste HDPE with other polymers, or even other grades of HDPE with a different molecular weight, makes it difficult to produce durable articles from recycled material. During later processing or use, phase separation or stratification can take place due to the lack of phase stability in the resulting blend. Even with sophisticated sorting equipment it is difficult to produce a quality level comparable with virgin HDPE material, because of the small differences between the physical properties of these two polymers (1).

A recent paper describes the reactive processing of a model blend of virgin HDPE and PP resulting in improved properties of the blend (2). The objective of the present work is to investigate in more detail the effects of the reactive extrusion process on the reactive blending of real waste polymer, obtained from shredded shampoo bottles composed of HDPE contaminated with an unknown quantity of PP. This waste stream was selected because it is representative of many bottle recycle streams. The most important factors that affect the morphology of the blend are the polymeric component ratio, the residence time and mixing in the extruder, and the reactant concentration. The effects of these factors on the mechanical properties were studied in the experiments. The reactive extrusion process was carried out in two types of high shear extruders: a self-wiping co-rotating twin-screw extruder and a Buss co-Kneader single-screw extruder. The resulting blends were characterized by tensile behavior, impact properties and thermal properties.

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EXPERIMENTAL

Raw Material and Additives

The waste polymer used in these experiments consisted of shredded and washed shampoo bottles provided by REKO, lot 2360, sample M043210. DSC was used to determine the relative melting enthalpies of both the PP and the HDPE fraction. From the melting enthalpies of the bottle waste, the HDPE fraction was determined to be 90% (± 2%). This material was compounded in the twin-screw extruder and the mechanical properties of compression-molded samples were determined as shown in *Table 1* (abreviations and symbols are explained in the **Nomenclature** section). The physical properties of the peroxides are given in *Table 2*. The monomers and monomer combinations were selected according to their volatility and initial homopolymerization velocity. Apart from monomers with a single reactive group, monomers with a combination of reactive groups were used. The physical properties of the monomers are taken from literature (3, 4) and given in *Table 3*. All components were used without further purification. Experiments with additional polypropylene were carried out with Montell Moplen Z30S, a homopolymer PP with a melt flow index (MFI) of 21 dg/min (2.16 kg, 190°C).

Extruders

The extrusion process was carried out in two different types of extruders: a co-rotating self-wiping twin-screw extruder and a Buss co-Kneader single-screw extruder. The co-rotating twin-screw extruder was an APV-Baker MPF50 with a diameter (D) of 50×10^{-3} m and an L/D of 24. The other extruder was a Buss laboratory co-Kneader PR-46, with a diameter of 46×10^{-3} m and an L/D of 15. The screw profiles of both extruders are shown in *Fig. 1*. The twin-screw extruder has 10 heated barrel sections, and in order to avoid bridging of polymer at the entrance, the feed zone was set at 120°C. The other heating zones of the twin-screw extruder were set at 180°C. The temperature of the polymer melt in the kneading zone was measured with three Fe/Co thermocouples. The Buss co-Kneader has three heating zones and a heated screw. The entrance zone was set at 120°C and the last two sections of the barrel as well as the screw temperature were set at 180°C. The polymer temperature in the Kneader was measured with eight Fe/Co thermocouples, which were inserted into kneading pins in the barrel. The shredded flakes were fed with a screw feeder into both extruders. The reactants were introduced at the same feed port as the solid feed, using a positive displacement pump. This method was chosen because addition of a combination of a monomer and peroxide to a heated barrel segment can lead to unwanted polymerization in the inlet tube. After extrusion, the mixture was frozen in liquid nitrogen in order to preserve the morphology and to stop any reactions from taking place. Because of the very low remaining concentration of initiating species (less than 4 ppm), further reactions during sample preparation will have no significant influence on mechanical properties.

Table 1. Material Properties of the REKO Bottle Waste.

Material Property	REKO
Tensile strength (MPa)	24.2
Elongation at break (%)	590
Young's modulus (MPa)	820
Impact strength (kJ/m^2)	7.5

Experimental Design

The objective was to elucidate the significance of the throughput, screw speed and the amount of reactants, so all three variables were varied during the experiments. In the co-rotating twin-screw extruder, experiments were performed with only one varying

Table 2. Properties of Peroxides Used.

Name	$k_0(s^{-1})$	E_A (J/mol)	δ (MPa)$^{0.5}$	M/n (g/mol)	$\tau_{1/2}$ @ 180°C(s)
Trigonox BPIC C75	2.49×10^{16}	150.15	14.2	88	5.7
Trigonox C	2.23×10^{16}	151.59	15.7	90	9.4
Trigonox 101	1.68×10^{16}	155.49	14.1	69.5	35
Trigonox T	1.17×10^{15}	146.98	16.0	104	52
Trigonox 145 E85	1.9×10^{15}	150.67	12.9	68.5	86

Table 3. Physical Properties of Monomers Used. 1: From (3), 2: From (4).

Monomer	$(k_p/k_t)^{0.5}$ (1/mol s)$^{0.5}$	δ (MPa)$^{0.5}$	Boiling Point (°C)
ST/MAH (85/15)	0.83[1]	19.4	≈155
ST	0.095[1]	18.4	145
BMA	0.57[1]	17.4	163
GMA	—	16.9	189
HEMA	—	20.3	205
HPMA	0.005[2]	19	240

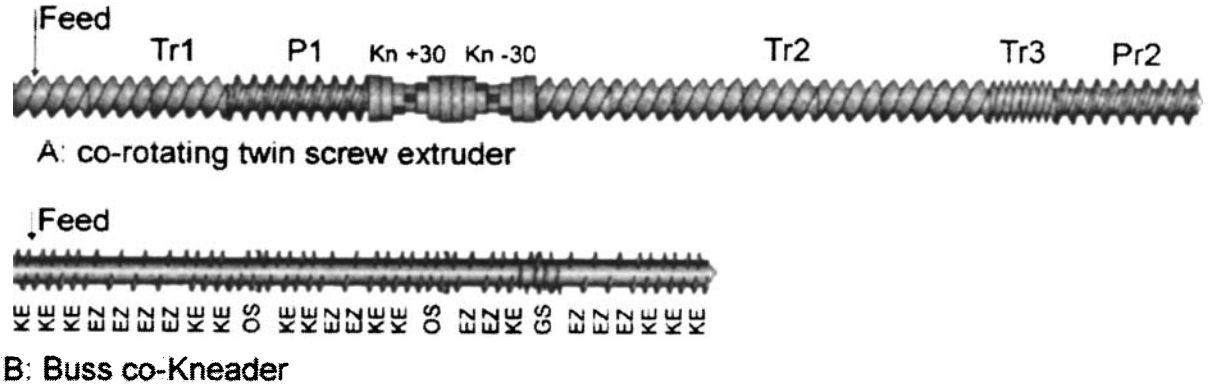


Fig. 1. A: Screw layout of the co-rotating extruder. Tr1: 0.225 m transporting section, Pr1: 0.15 m pressure buildup section, Kn. 30°: 0.09 m kneading section with 30° forwarding angle, Kn. -30°: 0.09 m kneading section with 30° reversed angle, Tr2: 0.415 m transporting section, Tr3: 0.075 m double pitched transporting section, Pr2: 0.15 m pressure buildup section. B: Screw layout of the Buss Kneader, EZ: conveying, KE: kneading, GS: closed channel, OS: baffle ring.

factor, keeping others constant. In the Buss co-Kneader, the experiments were carried out according to a statistical experimental design. The Box-Behnken scheme was selected, which is an orthogonal, rotatable surface design. In this design, the input factors were varied at three levels and the results were used to estimate all the main, quadratic, and two-way interaction effects. All 12 "edge" points (the black dots in *Fig. 2*) lie at equal distances from the center point, the open dot. The center point is measured three times to estimate the experimental error.

The order of the experiments was randomized to evenly spread the effects of factors not included in the experiment. The input parameters were screw speed, throughput and the amount of reactants. The reactants were n-BMA monomer with Trigonox BPIC with the ratio of monomer to initiator (M/I ratio) kept constant at 13 mol/mol. The responses of interest are the blend mechanical properties: impact strength, Young's modulus, strain at break and maximal stress. The data analysis was performed using StatGraphics Plus software. The general form of the resulting model is:

$$\text{Response} = a_0 + a_1 Q + a_2 N + a_3 R + a_{11} Q^2 + a_{22} N^2 + a_{33} R^2 + a_{12} Q \cdot N + a_{13} Q \cdot R + a_{23} N \cdot R \quad (1)$$

This model includes linear, interaction, and curvature effects for all input factors. With pareto analysis, the variables with a statistical significance at a 95% confidence level were retained in the model. With the results obtained according to this experimental design, the software was able to calculate a response model for impact strength, modulus and elongation at break.

Characterization

After extrusion, the extrudate was tested for mechanical, thermal, and viscoelastic properties. The mechanical properties were measured with compression-molded specimens. The polymer was pressed in a hydraulic press at 5 MPa at 180°C. The resulting specimens were tested for tensile modulus, tensile elongation at break and impact strength according to the standard ASTM procedures. Tensile behavior was measured on an Instron 4301 according to ASTM D1708 with a crosshead speed of 1.66×10^{-4} m/s. These tensile bars had a thickness of 2.0×10^{-3} m. The impact properties were measured according to ASTM D256 with notched bars of 4.0×10^{-3} m thickness. All tests were performed at room temperature and five to ten measurements were made to obtain averages. The resulting errors for the mechanical properties, as depicted by the error bars, are ±4% for the modulus measurements, ±9% for the impact measurements and ±9% for the measurements of the elongation at break. The dynamic mechanical properties of reactive compounded samples were measured in a Rheometrics RSA-2 in dual cantilever mode. The frequency was 1 Hz and the temperature rise was 0.033°C/s. The fraction of volatile components in a sample was measured with thermogravimetric analysis (TGA 7, Perkin Elmer). Calibration was performed with samples of known monomer content. This showed that the difference between the weight loss of a reactive extruded sample and a mechanical blend at 350°C is a good estimate of the remaining fraction of volatile materials in the blend.

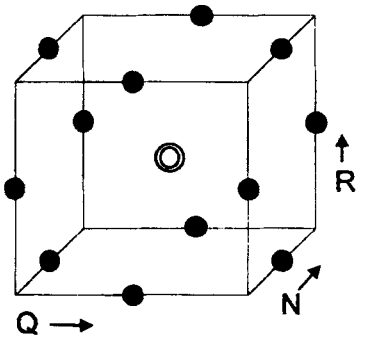


Fig. 2. Geometry of the Box-Behnken experimental design for the three variables Q (throughput), N (screw speed) and R (amount of reactants).

REACTIVE EXTRUSION IN A TWIN-SCREW EXTRUDER

Effect of Type of Peroxide

In a typical commingled bottle stream, a variety of contaminants can be found that influence the reactivity of the peroxide and the monomer but cannot be removed easily by washing. The concentration and reactivity of the peroxide will determine the conversion of the reactions within the limited residence time in the extruder. Apart from the half-lifetime and the concentration of peroxide, the nature of the resulting free radicals will play an important role. The most useful peroxides are those in which the primary free radical is sufficiently reactive to abstract hydrogen atoms from the polymer chain to form the corresponding macroradical. The relative reactivity or stability of the free radicals generated is related to the peroxide structure. In general, the lower the bond dissociation energy, the more stable and the less reactive is the corresponding radical (5).

The reactive extrusion experiments were carried out with a constant amount of 2 wt% of n-BMA monomer, and a variable amount of peroxide. Some of the initiators can form a different number of radicals. To be able to compare the different peroxides, a correction is made for the number of active oxygen atoms they can produce. The molar M/I ratio is then defined as the number of moles of monomer per mole of initiating oxygen. This means that for high M/I ratios, the relative concentration of initiator is low.

Figure 3 shows the effect of increasing the M/I ratio for several types of peroxides on the notched Izod impact strength. At high concentrations of peroxide, the surface of the extruded strand was very irregular, and the polymer was difficult to melt in the subsequent compression-molding step. The increased elasticity and different melting behavior can be attributed to crosslinking in the polyethylene phase. Decreasing the initiator concentration, resulting in an increase of the M/I ratio to 20 mol/mol, an optimum in impact strength can be observed. At higher M/I ratios, the concentration of reactive species is lower. This will lead to longer side chains and a low concentration of grafted groups onto the polymer.

Thermogravity experiments showed that at high M/I ratios, the conversion of monomer is low, and therefore not much improvement of the mechanical properties is to be expected. Treating the waste polymer with reactants can result in a 200% increase of the value for the impact strength, compared to the impact strength of the physical blend. The highest improvement is reached with the peroxide with the shortest half-lifetime. At an M/I ratio of 20, the impact properties have been found to improve according to the sequence: Trigonox BPIC > Trigonox 101 > Trigonox T ≈ Trigonox C > Trigonox 145. Apart from Trigonox C, this order matches the order of half-lifetimes (*Table 2*).

Trigonox C is a peroxyester and has a half-lifetime comparable to Trigonox BPIC, a peroxycarbonate. This means that decomposition of Trigonox C produces two types of radicals, one with a low energy and one with a high energy, overall making it less efficient in abstracting protons. The other initiators belong to the class of dialkyl peroxides. The starting point of the reaction is determined by the half-lifetime of the peroxide. Preferably, reactions should start before the kneading zone, and mixing should take place after sufficient monomer has been grafted on both phases. Another advantage of an early start of the reactions is also that the rate of evaporation of the monomer will be lower. When polymers enters the kneading zone, the concentration of peroxide should still be high enough to start reactions at the polymer interfaces, combining the grafts to form copolymer. These reactions reduce the interfacial tension between the phases, and this will lead to a smaller size of the dispersed phase.

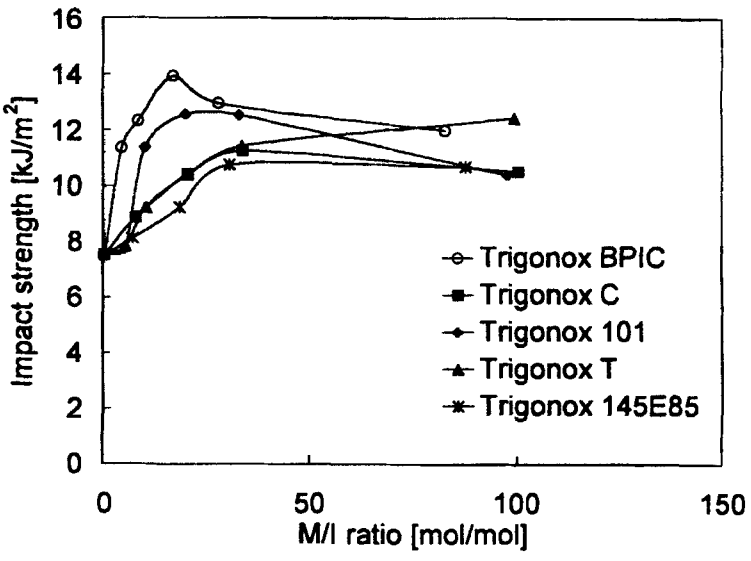


Fig. 3. Effect of molar M/I ratio on the notched Izod impact strength for bottle waste material; co-rotating twin-screw extruder, $Q = 3.58 \times 10^{-3}$ kg/s, N = 1.8 rps, 2 wt% n-BMA.

The residence time in the extruder is approximately 160 seconds, and with an average temperature of 180°C, this means that the conversion of Trigonox 145 is not complete, leading to less modification of the interface. In this case, most of the reactions will start at the end of the kneading zone, after all reactants are mixed through the polymer matrix. Decomposition of the peroxide will now mainly result in branching of the HDPE phase instead of formation of copolymers.

For the faster types of peroxide, the starting point of the reaction is shifted towards the entrance of the extruder. This reduces evaporation. Moreover, the concentration of initiator is still sufficiently high when all the material is molten, increasing the possibility of PE-PP graft reactions. The polymer is thoroughly mixed in the subsequent reversed kneading zone. This will result in smaller particles of dispersed phase having more interactions with the matrix phase and consequently improved properties. The most important criteria for the peroxide for enhancement of the impact strength are therefore the concentration and half-lifetime in relation to the residence time and the melting behavior in the extruder. To a lesser extent, also the chemical nature of the resulting primary free radicals plays a role.

The optimal molar M/I ratio using n-BMA as a monomer is in between 15 and 25 mol/mol. *Figure 4* shows the effect of the molar M/I ratio on the Young's modulus of bottle waste material. For all peroxides tested, the modulus shows a local minimum as a function of the M/I ratio. This minimum occurs at different M/I ratios, and is dependent on the type of peroxide. The minimum shifts to higher M/I ratios with increasing half-lifetime of the initiator. At low M/I ratios, crosslinking of the HDPE was observed. This results in brittle behavior of the polymer, because crosslinked points do not allow molecular pull-out to occur and so bond breakage must take place. The minimum in modulus does not coincide with the optimum in impact strength. For instance, for Trigonox BPIC, the minimum of the modulus occurs at a M/I ratio of 10 mol/mol, while the optimum in impact strength is reached with a M/I ratio of 22 mol/mol. The advantage of the reactive extrusion process is that the impact strength can be improved significantly, with only a slight reduction in the tensile modulus.

Effect of Type of Monomer

Apart from the type of peroxide, the type of monomer has an effect on the final properties of the product. The main functions of the monomer are reduction of unwanted side reactions such as degradation (e.g. PP) or crosslinking (e.g. PE). When the temperature in the extruder is high enough to start decomposition of the peroxide, reactions start to take place. After proton abstraction from a polymer chain, the macroradical can terminate by crosslinking, degradation or by reaction with a monomer resulting in a grafted monomer. The relative reaction rate of this grafting reaction versus the competing homopolymerization reaction will determine the effectiveness of the monomer. The monomer should not prefer one of the polymers present in the blend, which means that the solubility parameter of the monomer should be somewhere between those of the components in the blend.

Reactive extrusion experiments were carried out to test the effects of various monomers on the mechanical properties. Monomers were selected with different polymerization kinetics and solubility parameters as shown in *Table 3*. The solubility parameter (δ) was calculated using values of group contributions given by van Krevelen (6). To compare the effects of different monomers, the relative mechanical properties were calculated by dividing the value for a certain material property by the corresponding value of an extruded physical blend. The experiments were carried out with a constant weight percentage of monomer and

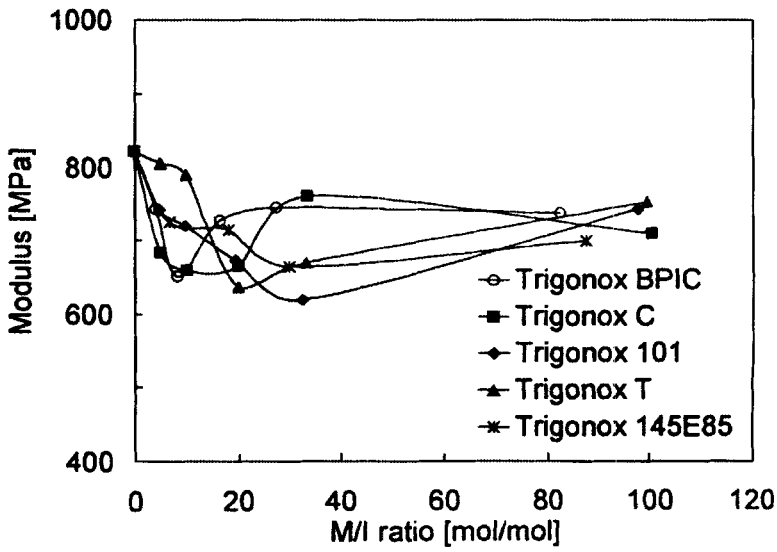


Fig. 4. Effect of molar M/I ratio on the Young's modulus of bottle waste material; co-rotating twin-screw extruder, $Q = 3.58 \times 10^{-3}$ kg/s, N = 1.8 rps, n-BMA = 2 wt %.

initiator added. The resulting M/I ratios are given in *Table 4*. *Figures 5* to *7* show the effect on the relative impact strength, the relative Young's modulus and the relative elongation at break for several different monomers in combination with three different peroxides.

The combined addition of a monomer and peroxide generally leads to a slight improvement of the impact strength of 30%–40%. Significant improvement of the impact strength of 50%–210% can be obtained with a combination of styrene and maleic anhydride (MAH), n-butyl methacrylate (n-BMA) and t-butylaminoethyl methacrylate (TBAEMA). Using MAH only resulted in a very high impact strength, mainly due to crosslinking of the HDPE phase. The use of the comonomer styrene results in a charge transfer complex, which can be grafted on both HDPE and PP, but side reactions such as crosslinking and degradation are reduced compared to the grafting of MAH only (7). Combined addition of MAH and styrene resulted in a product without detectable crosslinking and no discoloration. The formation of the homopolymer of MAH and other secondary reactions, responsible for off-colors, is inhibited in favor of the copolymerization of styrene and MAH.

Table 4. Molar M/I Ratios (mol/mol) for Experiments With Different Monomers and Initiators.

	Trigonox BPIC	Trigonox C	Trigonox T
ST/MAH	57	59	67
ST	56	58	66
BMA	41	43	48
GMA	41	42	48
HEMA	45	43	53
HPMA	41	42	48
TBAEMA	32	33	37

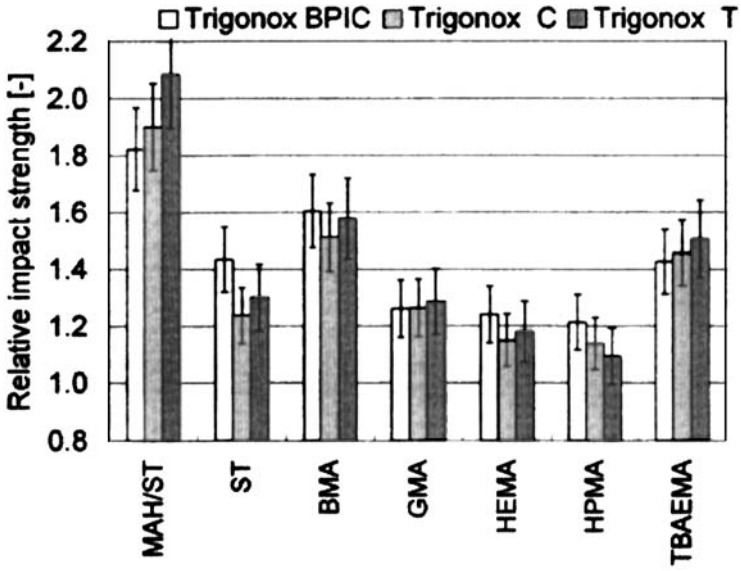


Fig. 5. Relative impact strength for different monomers and various peroxides. Monomer concentration is 2 wt% and peroxide concentration is 0.03 wt%.

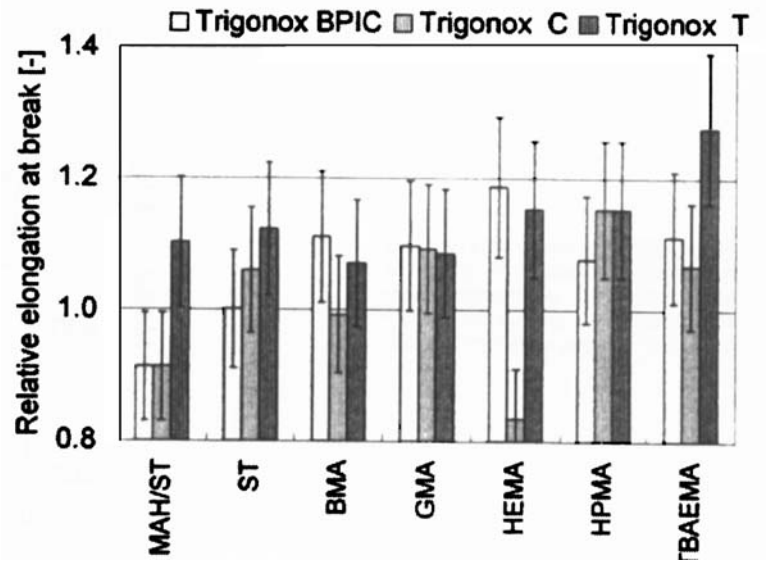


Fig. 6. Relative elongation at break for different monomers and various peroxides. Monomer concentration is 2 wt% and peroxide concentration 0.03 wt%.

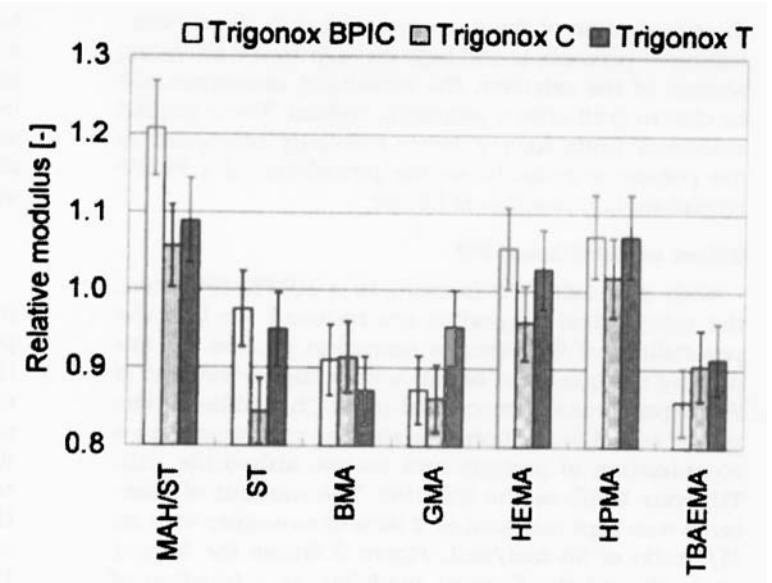


Fig. 7. Relative modulus for different types of monomer and various peroxides. Monomer concentration is 2 wt% and peroxide concentration is 0.03 wt%.

For the three peroxides used, the half-lifetime of the peroxide seems to be less important than the type of monomer added to the polymer. Within the experimental error, no significant influence was found. This can be attributed to the fact that the molar M/I ratio is 41–53 mol/mol and peroxide concentration is relatively low. Compared to *Fig. 3*, this is not the optimal M/I ratio. Moreover, at lower amounts of peroxide, the impact strength improvement does not follow a strict order of half-lifetimes. This is because Trigonox T is a dialkyl peroxide, which is more effective in abstracting protons at low concentrations than the other two peroxides. The effect of the different monomers on the ultimate elongation is less pronounced compared to the effects on the impact strength. The average improvement is 0%–10%. This indicates that crosslinking of the polyethylene is not the dominant toughening mechanism because this would result in reduction in the ultimate elongation. The ultimate elongation of the unmodified material already is 590%, and no significant trends for type of peroxide and monomer were observed.

The most significant improvement of the elongation at break was obtained with TBAEMA as the monomer and Trigonox T as the peroxide. This monomer is particularly interesting because vinyl monomers containing an amine functionality have a low toxicity and a high reactivity, leading to a higher monomer conversion. A reduction of the elongation at break was found for ST/MAH with Trigonox BPIC and Trigonox C, which is an indication for low levels of crosslinking.

The effects of the different monomers and peroxide on the relative modulus are shown in *Fig. 7*. As expected from the results in *Fig. 5*, the modulus is generally lower. The results obtained with n-BMA and TBAEMA show the largest drop in the modulus. Using the combination of styrene and maleic anhydride with Trigonox BPIC and Trigonox C, the Young's modulus is equal to or even higher than the modulus of unreacted material, which is another indication of low levels of crosslinking.

The reactant mixture is applied randomly to the polymer flakes at the feed entrance of the extruder. Polyethylene starts to soften at 90°C, and reactants will penetrate into the soft outer layer and the peroxide starts to decompose. At this stage, the reaction rate is low and the reactants will diffuse into the outer layer of the polymer pellet. At higher temperatures, the decomposition rate of the peroxide increases and reaction rates will increase. Because the rate of diffusion is now lower than the reaction rate, the reaction products will be formed mainly in the outer layer of the soft polymer granule. This reduces the loss of monomer due to evaporation. With still increasing temperature, the polyethylene and polypropylene will melt entirely and both phases will fuse together. For the formation of block copolymers between HDPE and PP, reactions should occur at the interface between both phases. The course of the reactions is now dependent on the decomposition rate of the peroxide and the relative velocity of the homopolymerization and the grafting reaction. The difference in solubility parameters of the polymer and the monomer or peroxide was not found to be related to the final mechanical properties, as grafting occurs before the mixing zone. The reactions are diffusion-limited, and the effect of the different solubility parameters between the monomers and the polymers is difficult to detect.

The major difference between styrene only and the combination of styrene/maleic anhydride is the reaction rate. Styrene has a low reaction rate and a relatively low boiling point. The combination of styrene/maleic anhydride has a similar boiling point, but the grafting rate is much higher (3). The reactions will start with copolymerization of styrene and maleic anhydride and grafting on both PP and PE. This reduces

the evaporation of the monomer. Because the concentration of peroxide is still high enough in the kneading section of the extruder, the remaining monomers will be able to graft onto a polymeric radical. These grafted monomer units have a lower reactivity compared to the polymeric radicals, so the probability of a PE-PP recombination reaction is higher.

Effect of Additional PP

With increasing PP fraction in a HDPE/PP blend, the mechanical properties are reduced. To test the possibilities of the reactive extrusion process for improving the quality of blends with a higher amount of PP, experiments were carried out with additional virgin PP added to the bottle waste. The reactants were a combination of styrene and maleic anhydride with Trigonox BPIC as the initiator. The amount of reactants was kept constant at 2 wt% of monomer with an M/I ratio of 55 mol/mol. *Figure 8* shows the impact strength and the Young's modulus as a function of the percentage of additional PP for both a physical blend and a reactive extruded blend. As expected, the results for the physical blend show that an increased amount of PP results in an increased Young's modulus and a strongly decreased impact strength and elongation at break. Processing the waste polymer with the reactants results in a 25% higher impact strength at low concentrations of additional PP, but decreases with increasing PP fraction. The modulus of the reactive extruded material is lower relative to the modulus of the physical blend and independent of the polypropylene fraction. Reactive extrusion with a mixture of 5% of additional PP results in similar properties compared to a physical blend without additional PP. An increased amount of PP results in a higher polymer/polymer interfacial area, so more compatibilizer has to be formed. Because the amount of reactants was kept constant, the relative amount of modified material in the blend decreases with increasing amount of PP. It can be concluded that the reactive extrusion process is sensitive to changes in feedstock composition. For different amounts of the dispersed phase, different amounts of reactants are necessary.

THERMAL PROPERTIES

Measurement of the thermal properties of the blend has proved to be useful in studying the structure of polymers in relation to their performance. With DMTA the material is deformed under a periodic force and the dynamic mechanical properties are obtained. The mechanical damping factor of the material as a function of the temperature is one of these properties. *Figure 9* shows damping factors (Tanδ), as a function of the temperature. The curve of the physical blend (A) is characteristic for a linear polyethylene. The Tanδ of HDPE has a maximum at −120°C called γ, which is ascribed to the glass transition temperature of the amorphous regions in the polyethylene. The next transition in linear polyethylene is the α transition at 50°C. The reactive extruded bottle waste blend (B) exhibits a different behavior. The Tanδ shows an increase between −90°C and −10°C. This so-called β-transition is usually seen only in branched polyethylene (LDPE). The increase is ascribed to movement of branching points in the amorphous phase (8). Kline *et al.* (9) attribute the relative height of this β-transition to the amount of short side chains. The increase should therefore be proportional to the number of grafted monomer units. The relative increase in Tanδ is highest for the sample with the highest impact strength. This means that toughening is caused by a combination of short chain branching by grafting of monomer

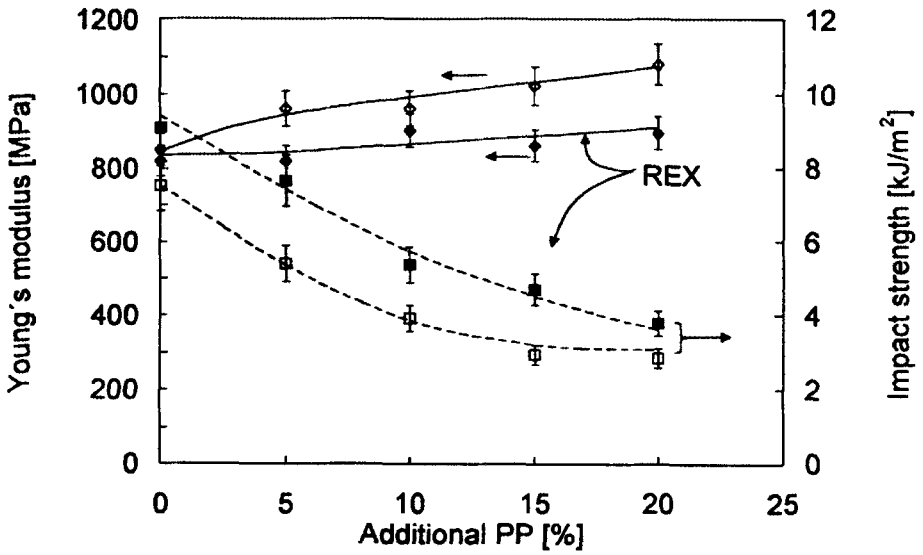


Fig. 8. Effect of increasing amount of polypropylene on the notched Izod impact strength (dotted lines) and Young's modulus (closed line) of bottle waste. Open symbols are physical mixtures, massive symbols are reactive extruded mixtures with 2 wt% ST/MAH and Trigonox BPIC. M/I = 55 mol/mol, Q = 3.6 × 10⁻³ kg/s, N = 1.8 rps.

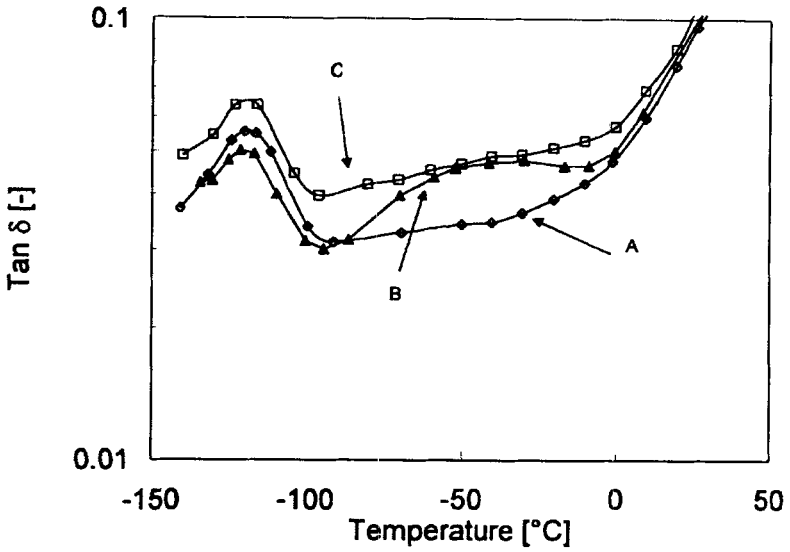


Fig. 9. Damping factor (Tan δ) as a function of temperature. A: physical blend, B: reactive blend with 0.15 wt% Trigonox BPIC and 2 wt% BMA, C: reactive blend with 0.3 wt% Trigonox BPIC and 2 wt% BMA. Co-rotating twin screw extruder, $Q = 3.6 \times 10^{-3}$ kg/s, $N = 1.8$ rps.

units, and an increase in long chain branching by recombination reactions of macroradicals. The DMTA spectrum of a reactive sample treated with monomer and a higher amount of peroxide (C) has a shape similar to that of a physical blend of the bottle waste but it is shifted upwards. Since crosslinking reactions lead to an increase in blend viscosity and therefore lead to a higher value for the Tanδ, these types of reactions appear to be dominant at higher levels of peroxide. This is to be expected because the rate of crosslinking of the HDPE phase increases linearly with the amount of peroxide (10), whereas the rate of grafting increases only by a power of 0.5 with initiator concentration.

PROCESSING WINDOW FOR THE CO-ROTATING TWIN-SCREW EXTRUDER

Changing the process conditions in an extruder will affect the reactive extrusion process. A change in screw speed or throughput will influence the residence time and the amount of mixing. These are important features when a reaction is performed during melt blending. In general, the residence time distribution is shifted to shorter times when Q or N increase. The next sections describe the effect of changes in extruder parameters. In this way, the most vital parameters for the reactive blending process can be determined. Because of the promising results obtained with styrene and MAH, this monomer combination was chosen for further experiments. Because also experiments at higher throughput and therefore shorter residence times were anticipated, Trigonox BPIC, a peroxide with a relatively short half-lifetime, has been chosen.

Processing Conditions

Increasing the throughput at constant screw speed has a small effect on the final properties of the product. As can be seen in *Fig. 10*, the elongation at break decreases from 850% to 650% with increasing throughput, while the impact strength is relatively constant at 11 kJ/m^2. The modulus increases from 820 to 920 MPa. Increasing the throughput causes a decrease in the mean residence time in the extruder from approximately 180 s to 90 s. Consequently, the conversion of monomer decreases from 90% to 70%, but more important, the conversion of the peroxide also decreases. This reduces the number of grafted groups and thus reduces the elongation at break.

The reaction time and temperature in the extruder determine the mechanical properties. The effective length of the section where reactions are taking place is determined by resulting rate of decomposition of the peroxide. At low throughput, softening of the polymer starts earlier in the extruder. This allows grafting reactions to start sooner, which results in a longer effective reaction length. After melting, the polymer melt is blended and the concentration of peroxide apparently is still sufficiently high to induce PE-PP grafting. The reaction is completed before the end of the kneading section, and owing to the higher mixing, this will result in smaller particles due to the interfacial modification.

The higher elongation at break is a clear indication of increased interaction between the phases at low deformation rates. At higher throughput, more material needs to be molten and melting is delayed. The reaction starts when all the polymer pellets are molten, so the effective reaction length is shorter, decreasing the number of grafted groups. Because of the mixing, the reactants are also distributed over the polymer melt, which means that the concentration of reactants at the polymer interface will be lower. Grafting at the interface becomes less likely and the peroxide will mostly cause local branching in the PE or degradation of the PP rather than formation of copolymer between these two phases. A small amount of branching will increase impact strength, but elongation at break is

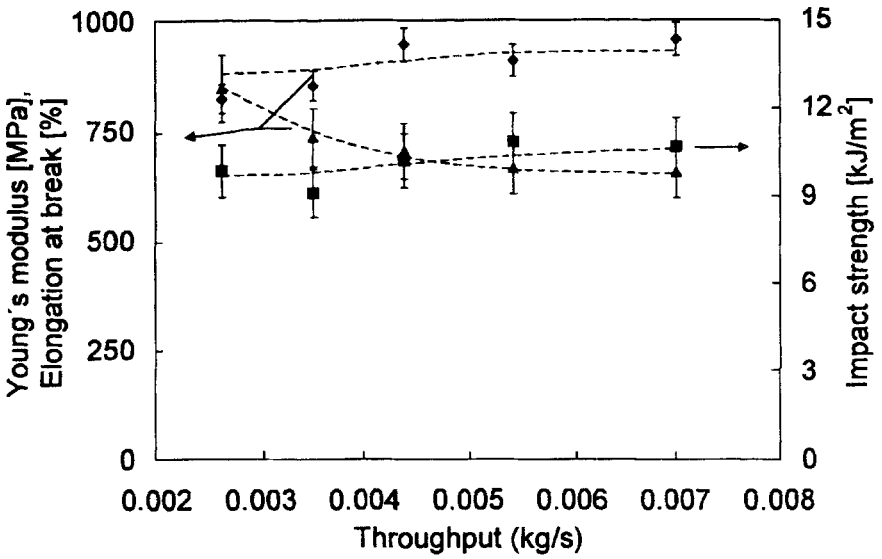


Fig. 10. Effect of variation of throughput in a co-rotating twin-screw extruder: elongation at break (▲), Young's modulus (◆) and impact strength (■), N = 1.8 rps, 2 wt%. ST/MAH with Trigonox BPIC, M/I = 55 mol/mol.

not improved because no interactions between the blend components are present.

Figure 11 shows the effects of increased screw speed on the modulus, impact strength and elongation at break at a constant throughput of 3.6×10^{-3} kg/s. Increasing the screw speed at constant throughput results not only in a improved mixing, but also a reduction in residence time of 144s at 2 rps to 120s at 7 rps. The conversion of the monomer is slightly reduced from 89% to 79%, but peroxide conversion is still practically complete. Both the impact strength and the elongation at break show a decrease with increasing screw speed. The modulus increases with screw speed. The impact strength of the sample obtained with a relatively high screw speed of 7 rps is equal to that of a physical blend, but the elongation at break is lower, and modulus is higher, suggesting that crosslinking of the HDPE phase occurred. At a low screw speed and throughput, the polymer flakes will melt, and grafting reactions will start at the outer surface of the polymer before the polymer is completely molten. After melting, the concentration of peroxide is still sufficiently high to induce PE-PP graft reactions at the interface. The amount of reaction and mixing is sufficient to improve the elongation at break.

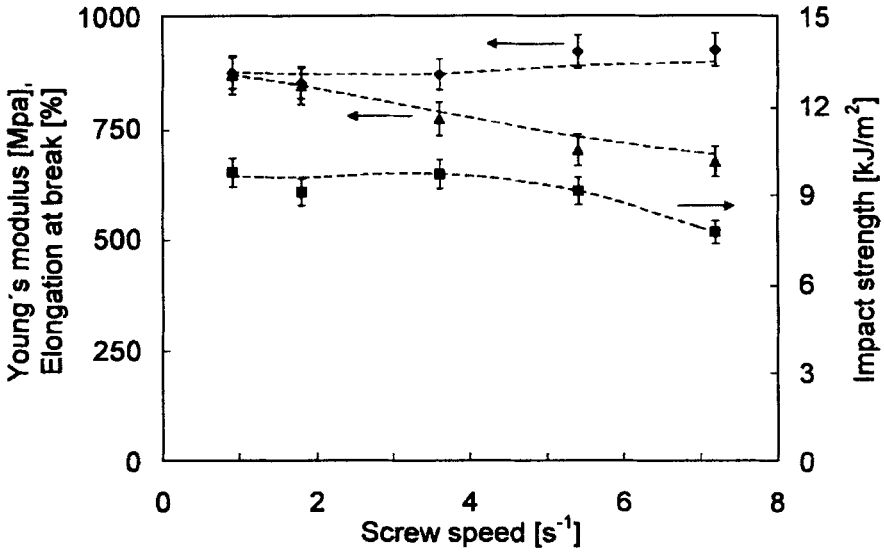


Fig. 11. Effect of variation of screw speed in a co-rotating twin-screw extruder elongation at break (▲) Young's modulus (◆) and impact strength (■), Q = 3.6×10^{-3} kg/s, 2 wt%. ST/MAH with Trigonox BPIC, M/I = 55 mol/mol.

A higher screw speed has a small effect on the residence time but increases the mechanical energy introduced to the polymer. This results in a very steep temperature rise of the polymer in the first barrel sections of the extruder. Because of the low degree of fill in the pressure section before the kneading section, reactants can evaporate, leaving less monomer available for grafting. Reaction now starts after all polymer has melted. Owing to more effective melt mixing, the reactants are distributed over the polymer melt, so the concentration of reactants at the interface will be lower. Moreover, because of the energy input, the temperature rise across the kneading section results in a high concentration of radicals, which will favor crosslinking. The specific throughput is defined as the ratio of throughput to screw speed, Q/N. This ratio characterizes the degree of fill and the intensity of mixing. Keeping the specific throughput constant results in equal mixing. Therefore, unlike a change in Q or N that affects the residence time and micromixing as well, changing the throughput at constant Q/N affects only the residence time. *Figure 12* shows the influence of throughput at constant specific throughput on the mechanical properties. The residence time decreases from 160 s to 40 s and the overall conversion of the monomer decreases from 90% to 82%. The modulus is unaffected by a change in the processing conditions, but the elongation at break decreases slightly with an increase in screw speed. Despite the decrease in conversion, the impact strength increases. Unlike the experiments at constant screw speed, the higher energy input results in a higher melt temperature. This counterbalances the negative effect of the shortened residence time at higher throughput. Reactions start shortly before the polymer enters the kneading zone, resulting in grafting on both phases. Because the mixing is sufficient, and the relative concentration of peroxide is still quite high at the entrance of the kneading zone, interfacial graft reactions are likely to occur. The milder processing conditions resulted in only a small temperature increase in the kneading section. This increases the grafting rate, but does not result in a high concentration of free radicals that cause crosslinking of the HDPE.

REACTIVE EXTRUSION IN THE BUSS CO-KNEADER

Apart from co-rotating twin screw extruders, the Buss co-Kneader is widely used in many reactive compounding operations (11). The co-Kneader offers excellent possibilities not only for homogenization and mixing but for control of the viscous temperature rise as well. The operating principle of the Buss co-Kneader is different from single-screw or twin-screw compounders (12). In general, it is considered as single-screw machine with twin-screw action. From the results in the twin-screw extruder, it was concluded that the residence time (throughput), mixing (screw speed), and the amount and type of reactants are important parameters in creating the blend morphology and corresponding mechanical properties.

From the experimental results in *Table 5*, the individual response models for impact strength, elongation at break, and modulus were calculated. The analysis for the impact strength was statistically significant and the correlation coefficient for the model is 93%. The average value for the impact strength was 11.2 kJ/m^2, which is significantly higher than the impact strength for a physical blend. Linear regression yielded the following equation:

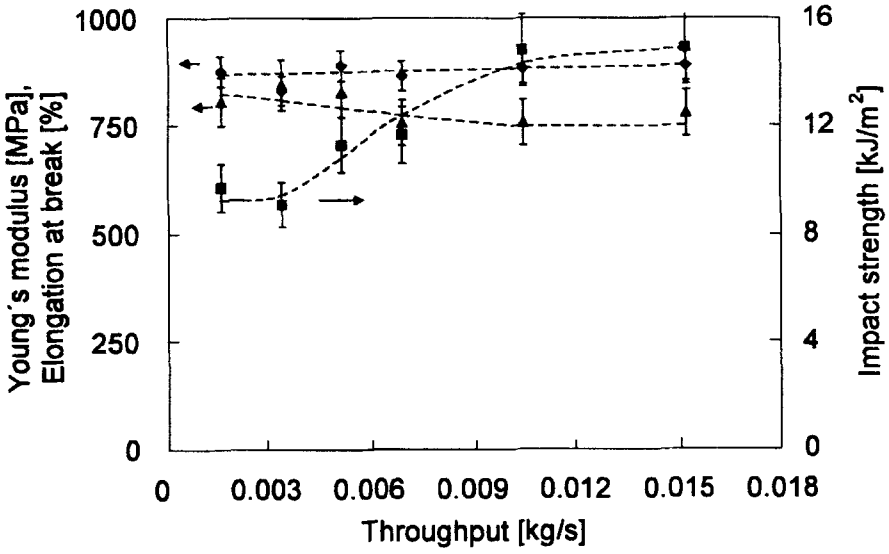


Fig. 12. Effect of variation of throughput at constant specific throughput in a co-rotating twin-screw extruder. Elongation at break (▲), Young's modulus (◆) and impact strength (■), Q/N = 0.002 kg.

Table 5. Extruder Settings for Experiments Performed With the Buss co-Kneader. Reactants Are n-BMA and Trigonox BPIC in an M/I Ratio of 13 mol/mol.

Screw speed (rps)	Throughput $\cdot 10^3$(kg/s)	Reactant (wt%)	Impact strength (kJ/m^2)	Young's modulus (MPa)	Strain at break (%)	Maximal stress (MPa)
3.16	4.16	4.74	15.1	723	835	24.1
3.16	2.80	3.23	10.3	763	707	26.3
3.16	1.38	5.06	13.2	762	605	24.0
1.66	1.38	2.99	12.5	766	581	23.7
1.66	2.80	1.47	9.7	897	—	27.8
1.66	2.80	3.37	10.3	776	568	27.0
4.66	4.16	3.19	10.8	757	699	26.8
3.16	1.38	1.44	14.9	784	765	24.0
1.66	2.80	4.98	10.2	829	560	24.2
3.16	4.16	1.36	9.7	915	652	25.5
4.66	1.38	3.72	12.9	706	729	26.9
3.16	2.80	3.19	10.7	759	689	25.4
1.66	4.16	3.27	10.2	875	617	25.1
4.66	2.80	4.98	11.3	714	722	24.5
4.66	2.80	1.45	9.8	790	640	25.6

$$\textit{Impact strength} = 20.2 - 8240\,Q + 3.27\,N - 1.65\,R + 939000\,Q^2 - 0.495\,N^2 + 738\,Q \cdot R \quad (2)$$

The elongation at break is sensitive to small differences in preparing the test samples. The correlation coefficient for the elongation at break was therefore only 88%. The average elongation at break is 712%, which is higher than the elongation at break of a physical mixture. The resulting model equation is:

$$\textit{Elongation at break} = 489 - 97100\,Q + 251\,N - 84.8\,R - 32.9\,N^2 + 33700\,Q \cdot R \quad (3)$$

Generally, both elongation at break and impact strength show a decrease with throughput and increase with amount of reactants. Both models also show an interaction term between throughput and reactant level. The most significant effects in both models are combinations of throughput and reactants. This means that residence time and concentration of reactant are the most important factors for the reactive extrusion process. The effect of increased screw speed is positive but the magnitude of this effect is smaller compared to the effects of the reactants. The elongation at break is more sensitive to changes in screw speed and thus mixing behavior. The screw speed shows an optimum as this reduces the residence time but increases the energy dissipation. The resulting increase in melt temperature increases the reaction rates.

Effects that contribute positively to the impact strength should cause a decrease in modulus. *Equation 4* indeed shows that this assumption is true. The equation for the fitted model of the modulus is:

$$\textit{Modulus} = 850 + 75000\,Q - 30.3\,N - 53.3\,R + 11.6\,R^2 - 16500\,Q \cdot R \quad (4)$$

The correlation coefficient is 92% and the average value is 764 MPa, which is only 7% lower than the modulus of a physical blend (*Table 1*). The largest positive effect on the modulus comes from an increase in throughput and screw speed. The amount of reactants and the interaction term of throughput and reactant level have a negative effect as expected. Like the results obtained in the twin-screw extruder, the residence time is the determining factor for the reactive compatibilization process. The amount of reactants contributes positively because of a higher amount of interfacial modification.

Processing Conditions

With *Eqs 2* to *4* the values for the Young's modulus, impact strength and elongation at break can be calculated at various levels of reactants. *Figure 13* shows the calculated Young's modulus and impact strength at a reactant level of 2 wt%. At this reactant concentration, the impact shows an optimum at intermediate screw speeds. At low screw speeds, the mixing is not sufficient, but at high screw speed, where the mixing is good, the residence time becomes too short. The effect of the diminished residence time is clearly more important than the amount of shear introduced to the polymer. Increasing the throughput reduces the average residence time and therefore the conversion of the reaction in the extruder. The mechanical properties of the blend obtained by reactive compounding in the Buss co-Kneader are comparable to the properties obtained in the twin-screw extruder. Because the effects of screw speed are relatively low, the amount of energy introduced and so the amount of mixing apparently is sufficient to obtain small domain sizes of PP throughout the range tested.

The elongation at break at low reactant level is shown in *Fig. 14*. The elongation at break shows a gradual decrease with throughput and an optimum at intermediate screw speed. For low screw speeds, the resulting material has a combination of a high modulus with a lower toughness, suggesting that crosslinking of the polyethylene phase takes place at these processing conditions. Melting and mixing of the polymer now occur later in the extruder. Most of the reaction will take place at the soft surface of the polymer flake. This will reduce the concentration of initiator left in

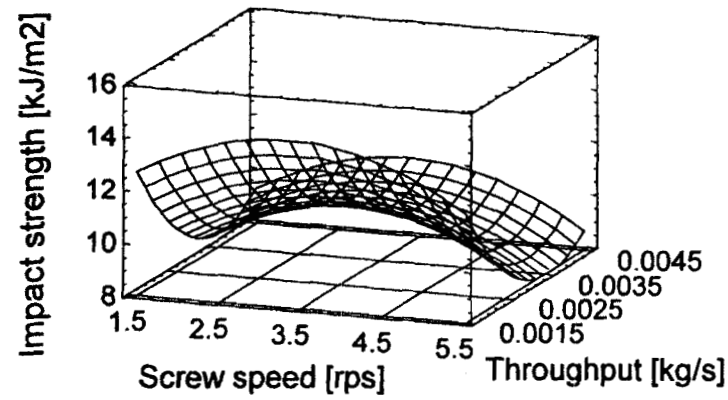


Fig. 13. Calculated Young's modulus and impact strength for varying throughput and screw speed at a reactant level of 2 wt%.

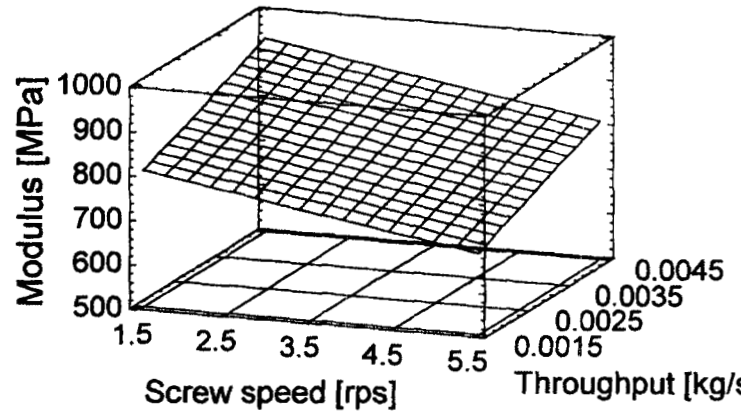
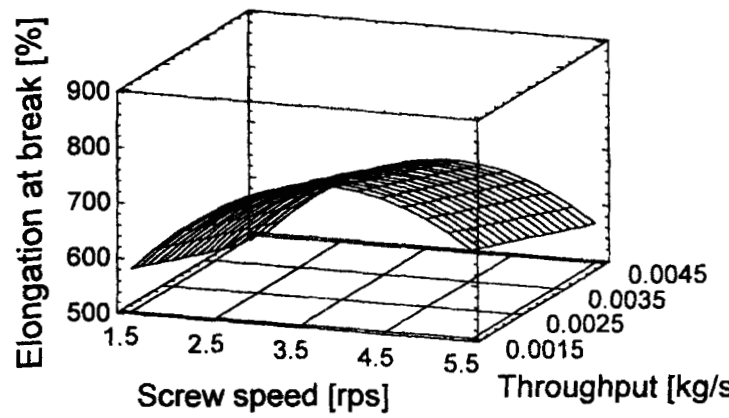


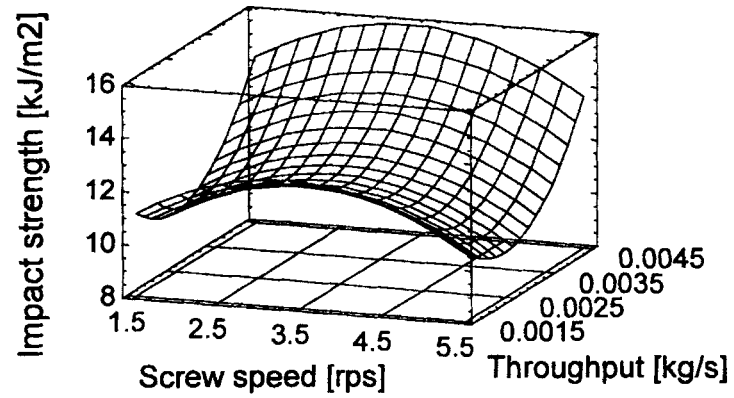
Fig. 14. Calculated elongation at break for varying throughput and screw speed at a reactant level of 2 wt%.



the mixing section, and reduces the possibility of reactions between the polyethylene and polypropylene. Because the degree of fill in the screw channel is lower, the monomer can also evaporate, reducing the maximal amount of grafted material.

For a higher amount of reactants (5 wt%), different results were obtained. *Figure 15* shows the Young's modulus and impact strength as a function of screw speed and throughput. A higher percentage of reactant leads to a further improvement of the toughness of the polymer blend, due to the increased percentage of grafted groups. The optimum toughness is reached at medium screw speed and high throughput. Both elongation at break and impact strength follow the same trend, indicating that the toughening mechanism is interfacial modification rather than polyethylene crosslinking. The modulus for these experiments is independent of the throughput and decreases with increasing screw speed.

The results of the experimental design shows that like the twin-screw extruder, the Buss co-Kneader can be used for the reactive compatibilization process.



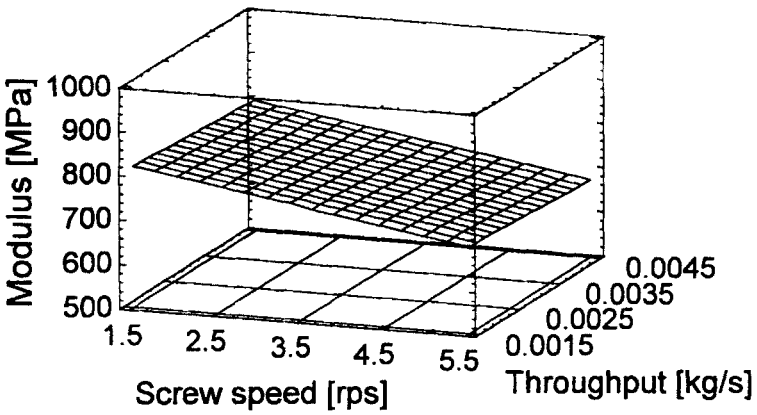


Fig. 15. Calculated Young's modulus and impact strength for varying throughput and screw speed at a reactant level of 5 wt%.

With the processing conditions used, the toughness is significantly improved compared to a physical mixture of shampoo bottle waste. The response of processing conditions at a similar reactant level of 2 wt% are different to changes in processing conditions in the twin-screw extruder. In the Buss co-Kneader, the residence time also has the largest effect on the toughness. The effect of screw speed shows an optimum. The effect of increased mixing is dominant at low screw speeds. At a higher screw speed, the influence of the decreased residence time becomes noticeable, and owing to a relatively large effect of the residence time, the toughness decreases. At a reactant level of 5 wt%, the effect of varying processing conditions is similar to the effects observed in the twin-screw extruder. A relatively higher concentration of reactants and high throughput is beneficial to the physical properties of the material. At a higher throughput, the degree of fill increases, which results in improved melting behavior in the extruder. Together with a higher concentration of reactive species, more compatibilizer will be formed.

The temperature profile in the Kneader for a screw speed of 1.66 rps and a reactant level of 3.2 wt% is shown in *Fig. 16*. Because of the heated barrel, the polymer melt temperature rises and the flakes start to melt. At a relative length of 0.25, all the polymer flakes are melted. At a relative length of the extruder of 0.5, a restriction ring (OS) is inserted in the barrel. The degree of fill of the channel is therefore higher, and the temperature of the melt drops as a result of heat transfer to the barrel. At the end of the extruder, the melt temperature also drops because of higher degree of fill, and increased heat transfer. The fact that the melt temperature dropped below the set temperature of the last zone could be attributed to nonuniform cooling effects in the oil-cooled extruder.

With StatGraphics, the temperature of each thermocouple was correlated to the three input factors screw speed, throughput, and reactant level. In the section up to a relative length of 0.2, the polymer temperature and the melting process is not affected by the amount of reactants but only by throughput and screw speed. From a relative length of 0.2 to 0.53, the melt temperature is increased with increasing amount of reactants and screw speed. Branching and crosslinking reactions will increase the viscosity and therefore the melt temperature, so in this section most of the reactions take place. After an extruder length of 0.53, effects of throughput determine the melt temperature, and screw speed is not affected significantly by the amount of reactants added. This means that the viscosity does not change any more. The highest impact

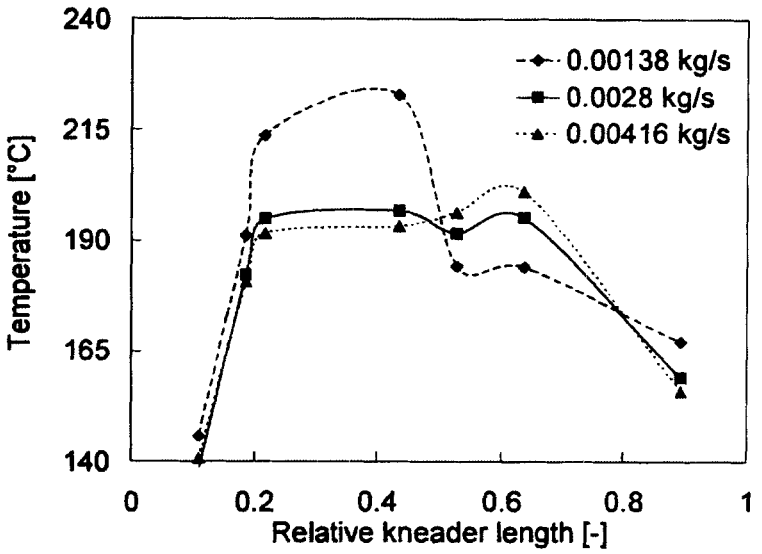


Fig. 16. Temperature profile in the Buss co-Kneader for low, medium, and high throughput. N = 1.66 rps, reactant level 3 wt%.

strength is reached with a higher melt temperature in the first section. This means that for high impact strength, reactions have to start early in the extruder. For a higher throughput, the start of the reaction is shifted towards the outlet of the extruder. If the reactions start after the polymer is melted completely, crosslinking of HDPE will be the dominant toughening mechanism. This also explains the higher viscous temperature rise at increasing throughput between 0.5 to 0.7 relative length.

CONCLUSIONS

Reactive extrusion with a combination of monomer and peroxide can be used successfully to improve the toughness of commingled waste polymer. Experiments performed with HDPE contaminated with 10% PP show that optimal impact properties can be reached with a relatively fast dialkyl peroxide and that its half-lifetime should be short in comparison with the residence time in the extruder. The monomer or monomer combination should have a high initial reaction rate, to prevent loss of monomer due to evaporation and to promote growth of grafted side chains on the polymer substrates present in the blend. The place in the extruder where the polymer starts to soften is considered to be the optimal starting point of the grafting reactions. However, the moment all polymer pellets fuse together, the initiator concentration should still be sufficiently high to promote formation of copolymers at the interface between the matrix and dispersed phase. Experiments with a combination of styrene, maleic anhydride and Trigonox BPIC showed that improvement of the toughness and impact strength of 180% to 200% could be obtained, with only a small reduction (7%) of the modulus.

The dynamic thermal characterization of the reactive processed material shows an additional thermal transition, which is usually found only in branched material. This is a clear indication that the toughening mechanism is branching within the material. The most likely explanation is the formation of a PE-PP copolymer.

The final monomer conversion was found to be between 65% and 90% and was dependent on processing conditions. This means that the resulting product has a residual monomer fraction of 5000 ppm, which can easily be reduced to acceptable levels by a devolatilization section.

The result of the reactive extrusion process is sensitive to inconsistencies in the feedstock composition. For PP fractions over 15%, a new optimization procedure in terms of reactant level is necessary. Another possibility that could lead to blends with interesting properties is incorporation of a disperse phase with a high modulus, for instance PS or PET.

The twin-screw extruder and the Buss co-Kneader can be used equally well for the reactive extrusion processes. The operating window of the co-Kneader was established with a statistical experimental design. This approach is useful to determine the responses of process conditions and reactant level on the final mechanical properties. The individual response maps for the properties of interest can be used to optimize blend properties and determine the most important effects for the reactive extrusion process.

NOMENCLATURE

BMA	n-Butylmethacrylate
DMTA	Dynamic Mechanical Thermal Analysis
GMA	Glycidylmethacrylate
HDPE	High density polyethylene
HEMA	Hydroxyethylmethacrylate
HPMA	Hydroxypropylmethacrylate
LDPE	Low density polyethylene
MAH	Maleic anhydride
PP	Polypropylene

ST	Styrene	
TBAEMA	t-Butylamino ethyl methacrylate	
TGA	Thermogravimetric analysis	
D	Diameter of the extruder screw	m
E_a	Activation energy	J/mol
$k_{p,t}$	Reaction rate constant	l/mol·s
L	Length of the extruder	m
M/I	Molar monomer to initiator ratio	mol/mol
N	Screw speed	s^{-1}
Q	Metered throughput	kg/s
R	Amount of reactants (weight %)	—
Tanδ	Damping factor	—
δ	Solubility parameter	$MPa^{0.5}$
$\tau_{1/2}$	Half-life time of the initiator	s

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